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Effect of Drop Size on the Degradation of VX in Concrete

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The effect of drop size on the degradation rate of VX, *O*-ethyl *S*-[2-(diisopropylamino)ethyl]methylphosphonothioate, in fresh concrete has been examined using ^{31}P NMR. Drops of neat VX, ranging in size from 4 μL to 0.2 μL, applied to small concrete coupons (8 mm × 15 mm) were observed to degrade at different rates, with the 1 μL and smaller drops reacting in less than 4 days, and the larger droplets reacting in less than 11 days. Additionally, 4 μL VX predissolved in hexane to evenly spread it over the concrete coupon likewise reacted faster, degrading in less than 5 days. The fresh concrete, less than 2 months old, exhibited significantly faster VX degradation for all drop sizes than that observed for "aged" concrete in a previous study where VX persisted for months. The enhanced reactivity of the "fresh" concrete for VX was maintained for at least a 1-year period. The pH of water containing crushed "fresh" and "aged" concrete was 10.0 and 9.0, respectively. The higher pH of the "fresh" concrete is one reason for its enhanced reactivity toward VX. An additional contribution to the enhanced reactivity of the "fresh" concrete is suggested by the increased mobility of its sorbed VX as evidenced by its significantly narrower peak in ^{31}P NMR spectra.

Introduction

The importance of drop sizes and their environmental persistence arises from the predicted size range of VX droplets reaching the ground following a military chemical attack, 0.01 to 2.0 μL,[1] and the need for battlefield commanders to know the severity and endurance of the hazard. For example, decisions must be made whether to expend time and resources performing wide-area decontamination or to determine if natural weathering, alone, will allow resumption of normal operations after an acceptable waiting period. Predictive models are required to allow commanders to make these battlefield decisions, and reliable data on agent persistence are crucial to the success of the models; thus the motivation for these ongoing studies.[2]

Recent studies examining the persistence of VX in concrete have produced seemingly widely different results.[3−5] Examining both small, neat 0.01-μL VX drops and solvent-assisted submonolayer applications of VX, Groenewold et al.[4,5] found that VX did not persist on concrete beyond a day or so. Yet in our preliminary study,[3] using the exact same concrete as Groenewold et al.,[4] large drops of VX on the order of several μL's persisted for more than a month. It was observed, however, that a small fraction of the applied VX did react relatively quickly within a few hours. The fraction of VX reacting quickly corresponded to about 1 monolayer, evidence that concrete does possess a reactive capacity of about 1 monolayer for VX. Therefore, the idea of a reactive concrete surface with a capacity limited to about 1 monolayer for VX that becomes overwhelmed by large droplets reconciles our results with those of Groenewold et al.[4,5]

Yang et al.[6] have shown that VX undergoes a slow, but selective, hydrolysis in water to yield nontoxic ethyl methylphophonate (EMPA) as shown in Scheme 1. On the other hand, basic hydrolysis is nonselective, yielding up to 22% of the toxic *S*-[2-(diisopropylamino)ethyl]-methylphonothioate (EA-2192).[7] In our preliminary study[3] we noted that VX degradation on the aged concrete examined was selective for EMPA, as EA-2192 was not detected by ^{31}P NMR. Using IT-SIMS, Groenewold et al.[5] also did not detect any EA-2192 formation on concrete.

In the current study, the persistence of various drop sizes of VX is examined on fresh concrete and these results are compared to those of the preliminary study. ^{31}P NMR is again used to monitor the degradation of VX and the emergence of the ethyl methylphosphonate (EMPA) product.

Experimental Section

Concrete. Fresh concrete was prepared using Quikrete concrete mix. As small coupons were desired, large aggregate was removed using a #10 sieve. The removed aggregate comprised about 43 wt % of the original concrete mix. The remaining concrete mix was mixed with water and cast into 8.5 cm × 12 cm × 1.4 cm slabs using a polyethylene mold. The freshly poured slabs were placed in sealed "Zip-loc" polyethylene bags for 2 weeks to prevent excessive moisture loss during curing. At the end of the 2-week period, the slabs, still visibly moist, were removed from their bags and allowed to air-dry. After an additional 2 weeks, the slabs were cut using a diamond-tipped circular saw to produce 8 mm × 2 mm × 15 mm coupons weighing about 0.5 g each. The size of the coupons was dictated by the inner dimensions (ca. 9 mm) of a standard 10-mm NMR tube (Wilmad Glass Company, Inc.) and the detector region (ca. 15 mm) of a standard 10-mm Varian NMR probe.

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14. ABSTRACT
The effect of drop size on the degradation rate of VX in fresh concrete is examined using 31P NMR. Drops of neat VX, ranging in size from 4 to 0.2 μL, applied to small concrete coupons degrade at different rates, with the 1 uL and smaller drops reacting in less than 4 days, and the larger drops reacting in less than 11 days. The fresh concrete, less than 2 months old, exhibits significantly faster VX degradation than that observed for aged concrete examined in a previous study. The enhanced reactivity of fresh concrete is attributed to its higher pH and increased mobility afforded to sorbed VX.

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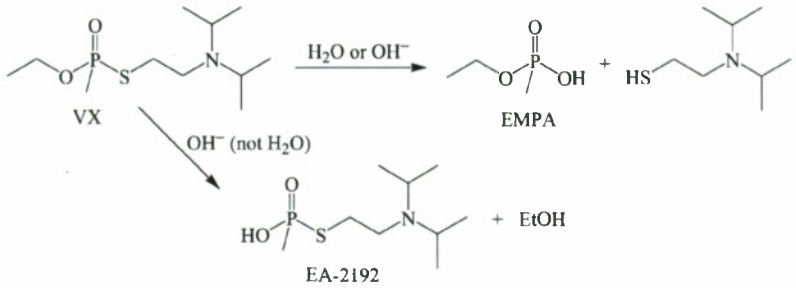
Scheme 1



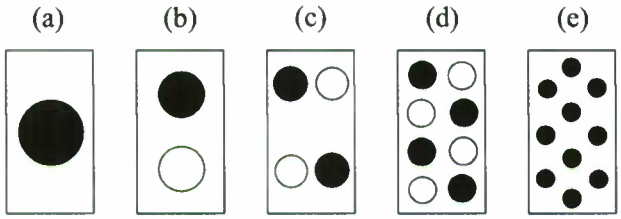


Figure 1. Patterns of neat VX drops applied to concrete coupons: (a) 1 4-μL drop, (b) 2 2-μL drops, (c) 4 1-μL drops, (d) 8 0.5-μL drops, and (c) 20 0.2 μL drops. Closed circles represent drops applied to the top face; open circles represent drops deposited on the bottom face. In (e), the same pattern was used on the bottom face; open circles have been omitted for clarity.

Concrete Analyses. The pH of the fresh and aged (from the preliminary study[3]) concretes was assessed by making a slurry of ca. 0.1 g of crushed concrete with 2 mL of water and measuring the pH of the water with pH indicating strips (EM Science). The water content of the two concretes was assessed by drying 0.4 g pieces for 24 h at 150 °C.

NMR. ^{31}P NMR spectra were obtained using "solution conditions" on Varian Unityplus and INOVA 400 NMR spectrometers using standard Varian 10-mm solution probes as previously described.[3] It was found that for VX sorbed on the "fresh" concrete used in the current study that ^{31}P NMR peaks for VX and EMPA were partially resolved, thus obviating the need for Magic-Angle Spinning (MAS) NMR (MAS was needed to resolve these peaks in the preliminary study[3]). ^{31}P T_1's for VX and EMPA sorbed on the concrete coupons were 0.2 to 0.3 s, thus allowing spectra to be obtained within 14 min using 90° pulses, 2-s recycle delays, and 200 to 400 scans. Chemical shifts were referenced to external 85% H_3PO_4 (0 ppm).

Sample Preparation and Analysis. *Caution: The following should only be performed by trained personnel using applicable safety procedures.* Neat drops of VX in the size range 4 μL to 0.5 μL were applied to the concrete coupons using a 10-μL syringe. The smallest drops of VX, 0.2 μL, were applied to the concrete coupons using a 10-μL syringe and a Hamilton Model PB600-1 Repeating Dispenser. The number of drops of each size was varied to maintain a total amount of 4 μL, that is, 1 4-μL, 2 2-μL, 4 1-μL, 8 0.5-μL, and 20 0.2-μL. To minimize overlap, the drops were applied according to the patterns shown in Figure 1.

To load a concrete coupon using VX dissolved in a solvent, a stock solution of VX in hexane was prepared such that 20 μL of the solution contained 4 μL of VX. A 20-μL volume of the stock solution was then applied to the front and back of the concrete coupon. The hexane, which did not quite cover the entire front/back faces of the coupon, rapidly evaporated within a few seconds, as evidenced by the dry appearance of the concrete. In contrast, the neat VX drops persisted in their "wet" appearance for at least several minutes.

Following application of the VX drop(s), the concrete coupon was placed into a 10-mm NMR tube, which was fitted with its plastic cap and then sealed with Parafilm. ^{31}P NMR spectra were taken periodically to monitor the decomposition of the VX.

Results and Discussion

^{31}P NMR spectra obtained for VX drops of sizes 4, 2, 1, 0.5, and 0.2 μL applied to 8 mm × 2 mm × 15 mm fresh concrete coupons (according to Figure 1) are shown in Figure 2. The "fresh" concrete was 2 months old when this experiment was conducted. The ^{31}P NMR spectra yield overlapping peaks for VX (ca. 63 ppm) and EMPA (ca. 28 ppm), and lines have been added to the spectra to aid the reader in discerning these peaks. It is observed in all cases that VX slowly decomposes to EMPA over the course of several days. However, there are significant differences in the decomposition rates depending on drop size. Close inspection of the spectra reveal that after 4 days, considerable VX remains for the 4-μL drop sample (Figure 2d); perhaps a small amount of residual VX is evident as a shoulder for the 2-μL drop sample (Figure 2i); but no residual VX is evident for the 1 μL and smaller drop samples (Figures 2n, s, x). Thus, the smaller drops react considerably faster than the larger drops.

It should be noted that for each drop size, the final area of the EMPA peak is only about half that of the starting VX peak. This apparent decrease in the amount of expected EMPA is not due to T_1 effects, as sorbed EMPA possesses a much shorter T_1 than sorbed VX (0.039 vs 0.26 s). The extremely short T_1 observed for sorbed EMPA strongly suggests that it is influenced by relaxation at paramagnetic centers. Indeed, concrete is known to contain paramagnetic iron oxides. At present, we speculate that it is the reaction of EMPA with iron oxides, leading to the formation of paramagnetic iron phosphonates (in the same manner that EMPA forms aluminophosphonates on alumina[9]) and the resultant extremely broad NMR lines for bound EMPA, that is responsible for the approximate 50% decrease in the amount of expected EMPA.

The effect of using a solvent (hexane) to uniformly spread 4 μL of VX across a concrete coupon on the reactivity was also assessed. At the time of this experiment, the "fresh" concrete had aged for 14 months. Thus, a control experiment using a single 4-μL VX drop was also employed to determine any changes in the concrete reactivity as a result of the 14-month aging period. ^{31}P NMR spectra obtained for these two samples are shown in Figure 3. The decomposition rate of the single 4-μL VX drop shows that the reactivity of the "fresh" concrete has been maintained, even after aging for 14 months. Major amounts of VX remain after 2 days (Figure 3c); some remaining VX is evident as a slight shoulder after 6 days (Figure 3d), but no VX remains after 9 days (Figure 3e). In contrast to the behavior of the neat 4-μL drop, VX spread across the surface using 20 μL of a hexane solution containing 4 μL VX reacted considerably faster: only a small amount of VX is apparent as a shoulder after just 2 days (Figure 3h) and no residual shoulder is evident after 5 days (Figure 3i). Thus, the solvent-spread VX reacts as quickly as the smaller drop sizes discussed above. Future work will

(8) Assuming molecular area of 79 Å^2 for VX.[3]

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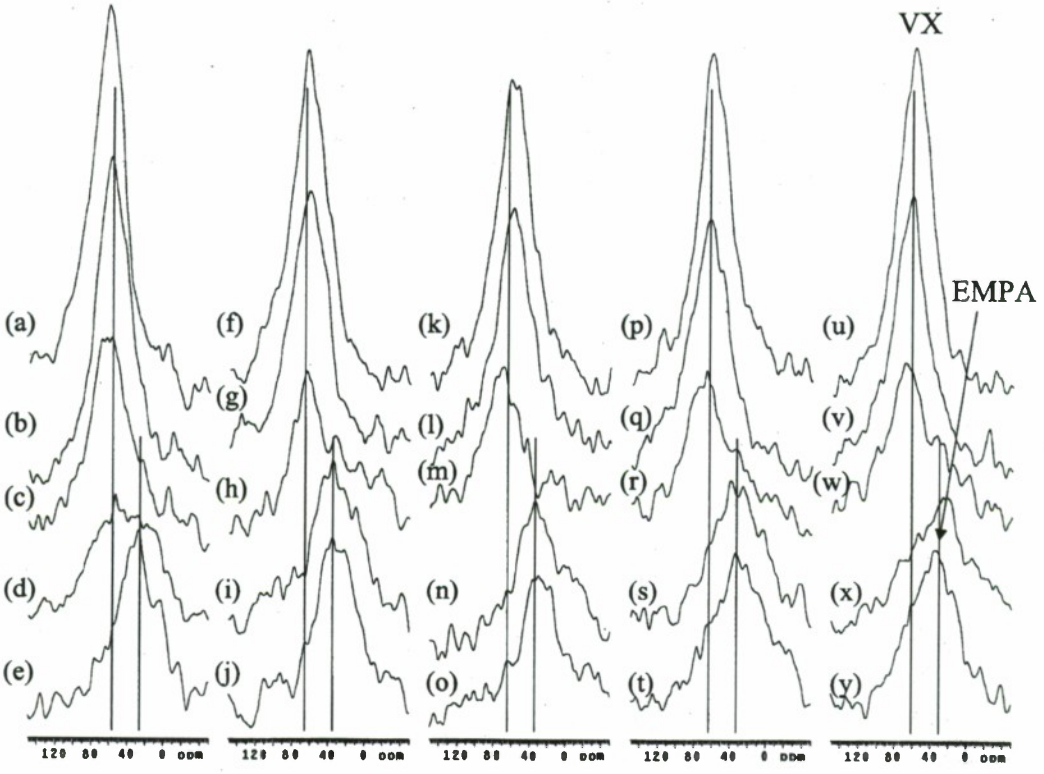

Figure 2. Selected ^{31}P NMR spectra obtained for VX added to concrete coupons at (top to bottom) 1 h, 5 h, 29 h, 4 days, and 11 days: 1 4-μL drop (a–e), 2 2-μL drops (f–j), 4 1-μL drops (k–o), 8 0.5-μL drops (p–t), and 20 0.2-μL drops (u–y).

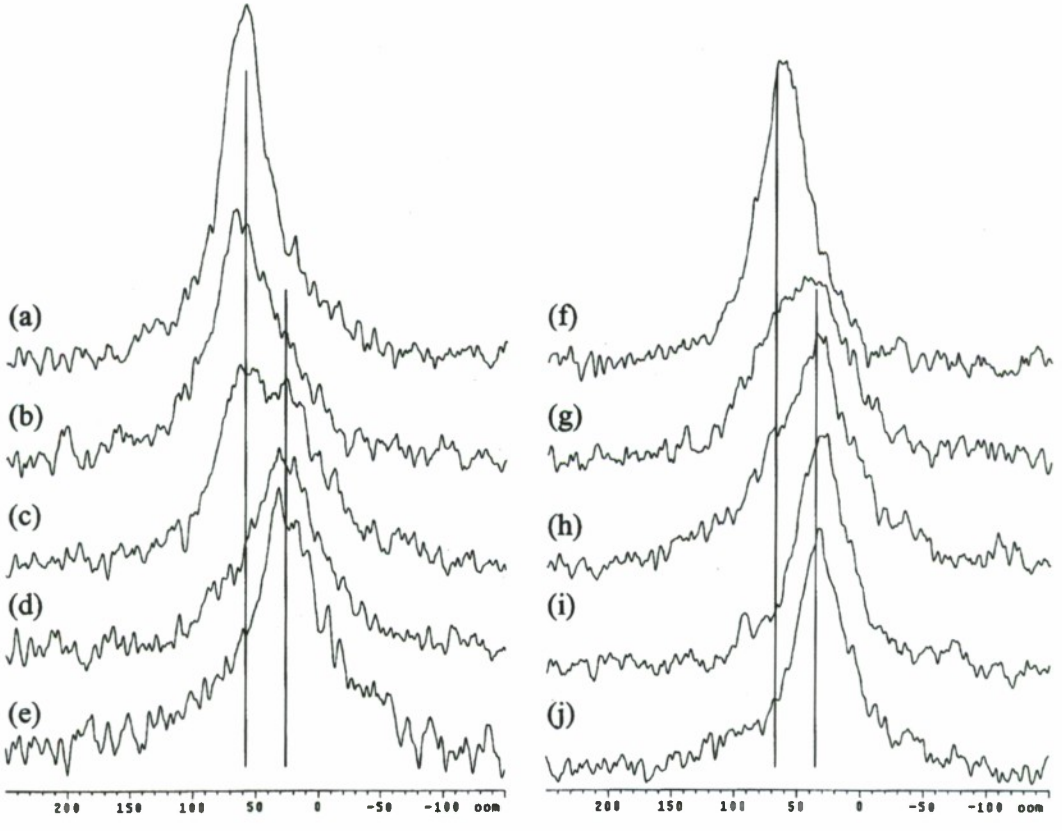

Figure 3. Selected ^{31}P NMR spectra obtained for 1 4-μL VX drop added to a concrete coupon at 12 min, 1 day, 2 days, 6 days, and 9 days (a–e, respectively); and 20 μL of hexane solution containing 4 μL VX added to a concrete coupon at 11 min, 1 day, 2 days, 5 days, and 8 days (f–j, respectively).

Table 1. Liquid Drop Diameters, Spread Diameters, and Local Contamination Densities/Monolayers for Various Drop Sizes

drop size (μL)	4	2	1	0.5	0.2	0.01[a]	solvent-spread[b]
drop diameter (mm)	2.0	1.6	1.2	0.98	0.73	0.027	-
spread diameter (mm)	7.0	5.6	4.2	3.4	2.6	0.095	-
local contamination density (g/m^2)	105	80	71	55	38	14	17[c]
# local monolayers[d] (upper limit)	1.8×10^5	1.4×10^5	1.3×10^5	9.8×10^4	6.7×10^4	1.9×10^4	3.0×10^4

[a] The 0.01-μL drop size was not studied; it is included only for illustrative purposes. [b] A 4-μL volume of VX spread across the concrete coupon using hexane; diameters do not apply. [c] The local contamination density of the solvent-spread sample is equal to the global contamination density of 17 g/m^2 (see text). [d] Local value based on amount of VX deposited on the "local" area under the spread drop.

involve examining very small droplets of VX down to, and including, the 0.01-μL size considered to be at the lower end of the threat range.[1]

Drop Size Considerations. A drop impacting a surface will tend to spread across the surface, with the "spread diameter" being greater than the diameter of the incipient spherical liquid drop. Of course, drops of various sizes will afford different spread diameters. The differing spread diameters offer a way to understand the observed reaction rates by considering their effect on the "local" contamination density vs the normally considered "global" contamination density, that is, the amount of agent deposited over a given area. For this exercise, the "global" contamination density is defined as the total amount of VX, 4 μL or 4 mg (liquid density ca. 1.0), applied to the total available area of the concrete coupon: 8 mm × 15 mm × 2 = 240 mm^2 (counting the front and back of the coupon, but not the sides). Combining these values yields a *global* contamination density of 17 g/m^2 for all the samples studied. However, it is clear from the drop patterns shown in Figure 1 that the applied VX drops do not cover the entire available area on the front and back of the concrete coupons (the solvent-spread sample is a notable exception, see below). In fact, the applied VX only occupies the area beneath its spread drop(s). The relative sizes of the spread drops depicted in Figure 1 are drawn roughly to scale as those actually observed. The spread diameter of the 4-μL drop was easily estimated as it did not quite touch the sides of the 8-mm-wide coupon. Thus, its spread diameter is estimated to be about 7 mm. The spread diameters of the rest of the drops are then calculated from this 7-mm estimated value by assuming the spread diameter is in direct proportion to the diameters of the nascent liquid drops. These values are summarized in Table 1. Although not examined in the current study, values for the noteworthy (see above) 0.01-μL size drop are also calculated and included for comparison. It should be noted that in the case of the solvent-spread sample, the local contamination density does equal the global contamination density as the VX is evenly distributed over the entire surface with no bare spots.

It is clear from the values in Table 1 that for large droplets the local contamination density greatly exceeds the global contamination density. Thus, the slow reactivity of the large droplets relative to the smaller drops is easily rationalized on this basis, that is, their region of the surface is more heavily contaminated. Conversely, the smaller droplets afford lighter surface contamination and, therefore, react quicker. It should be noted that for exceedingly small drops, the local contamination density should approach the global contamination density. This is shown to be the case for the hypothetical 0.01-μL drops, which are calculated to afford a 14-g/m^2 local contamination density, gratifyingly close to the global contamination density of 17 g/m^2. The closeness of these values shows that estimates for the spread-diameters of the drops are quite good.

Finally, it is also possible to relate the "local" contamination densities to monolayers. In the study by Groenewold et al.,[4] dilute VX solutions were employed to deposit extremely low amounts of VX on concrete corresponding to 0.04 to 0.0004 monolayers. For the current study, assuming a typical surface area of 4 m^2/g for the concrete coupons and that the 4 μL of deposited VX has evenly distributed itself throughout all the available surface area of the ca. 0.5 g coupon, the loading would be equivalent to 3.6 monolayers.[8] However, this is only a lower limit for the true number of monolayers as it is quite obvious from the reaction behavior of the drops that an even distribution of VX over all available surface area does not occur, at least not within the time it takes the drops to react. Therefore, the actual number of monolayers within the local contamination area of a spread drop is considerably higher. An upper limit estimate for the true number of monolayers can be obtained by considering the spread areas of the various VX drop sizes. Calculated upper limits of these "local" monolayers are given in Table 1. As with local contamination density, the local number of monolayers can be exceedingly high for the larger drops, but approach the value achieved for the solvent spread sample for the smaller drops. Of course, it is precisely the large number of monolayers associated with the finite drop sizes that gives rise to extended VX persistence. Infinitely small drops or minute amounts of VX deposited in submonolayer fashion do react quickly with the limited surface-reaction capacity of concrete, being on the order of one monolayer.[3]

Reactivity of Fresh vs Aged Concrete. VX is observed to decompose considerably faster on the "fresh" concrete used in the current study, even after aging for 14 months, compared to the aged concrete used in the preliminary study. That is, VX decomposed within several days on the "fresh" concrete, but persisted for several months on the aged concrete. At least two major factors appear to be contributing to the radically different reactivity of these concretes: pH and the mobility of the sorbed VX. The pH of a water slurry of crushed, "fresh" concrete (after aging for 19 months) was measured to be around 10, but that of the aged concrete was only around 9. Also, the "fresh" concrete had significantly narrower ^{31}P NMR lines for VX and EMPA compared to the aged concrete (narrower lines are indicative of greater molecular mobility). VX hydrolysis is enhanced at higher pH, and higher molecular mobility would facilitate diffusion within the concrete matrix, again resulting in an enhanced rate of hydrolysis. Sorbed water, one obvious reason for the increased mobility, does not appear to be a factor as the "fresh" and "aged" concretes both possessed similar amounts of water, about 2 wt % and 3 wt %, respectively. A more likely cause of the increased mobility is the protonation state of the sorbed VX. With a pK_a of 8.6,[6] VX would be more completely "free-based" on the fresh concrete (pH 10) than on the aged concrete (pH 9); thus allowing for greater mobility. The suspected pH-dependent mobility change observed for sorbed VX is in agreement with our speculation on the protonated nature of sorbed

VX on the aged concrete noted in the previous study.[3] Finally, it should be noted that high pH conditions favor the formation of toxic EA-2192 during VX hydrolysis. The current experiments did not employ MAS NMR, and without the improved resolution provided by this technique, EA-2192 would not have been detected. Further studies with high-pH concretes are planned, and MAS NMR will be used to determine if EA-2192 formation occurs.

Implications for VX Persistence and Battlefield Operations. Commanders in the field require knowledge of agent persistency to make informed, operational decisions in the advent of a chemical attack. Of primary concern is getting personnel into protective gear or into CB (Chem-Bio)-protected buildings, shelters, and vehicles. But, such protective gear and measures are quite cumbersome and will severely curtail operations. It is imperative that the contamination be alleviated to allow resumption of normal operations. Natural weathering tends to reduce contamination without anyone having to lift a finger. However, depending on the severity of contamination and its persistence, weathering may be insufficient to allow restoration of normal operations within a reasonable period of time. Indeed, if life-threatening contamination is to persist for extended periods, it may be warranted to expend time and effort performing wide-area decontamination. Predictive models for agent persistence currently under development will allow commanders to make informed decisions to both preserve the lives of soldiers and to fully restore battlefield operations as quickly and efficiently as possible. Besides the normal factors to be included in the model, that is, temperature, wind speed, humidity, precipitation, etc., the current results show considerable dependence of VX persistence on drop size. Thus, predictive models should also include drop size just like any other variable. To adequately implement predictive models in battlefield situations, it may be crucial to precisely know the sizes of agent drops reaching the ground in the advent of an attack, as the size will directly impact the persistence. This potential requirement will place severe demands on detector development, where not only would the precise agent and concentration have to be identified, but also the size(s) of the settling drops.

Conclusions

VX is observed to decompose relatively rapidly on the fresh concrete examined in the current study. The concrete possessed a rather high pH (pH 10) and also afforded relatively facile mobility for sorbed VX and EMPA product as evidenced by rather narrow lines in ^{31}P NMR spectra. Both of these factors are ascribed to the enhanced VX reactivity. Water content did not appear to play a role in the increased mobility as the fresh concrete contained a similar amount of water as the aged concrete examined in a previous study. Rather, a more plausible explanation for the apparent increased mobility of the sorbed VX on the fresh concrete is attributed to "free-basing" of the VX (pK_a = 8.6) at the higher pH of the fresh concrete. The decomposition rate of VX was quite dependent on droplet size, with 4 and 2-μL droplets reacting considerably slower than 1, 0.5, and 0.2-μL droplets. Finally, using hexane solvent to spread VX uniformly across the surface of concrete resulted in a reaction rate comparable to the small droplets.

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